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(71) Applicant : **MOLI ENERGY (1990) LIMITED**  
20000 Stewart Crescent  
Maple Ridge, B.C., V2X 9E7 (CA)

(72) Inventor : **Dahn, Jeffrey Raymond**  
17127 - 80th Avenue  
Surrey, B.C. V4N 3G4 (CA)  
Inventor : **Rossen, Erik**  
1480 Kilmer Road  
North Vancouver, B.C. V7K 1R2 (CA)  
Inventor : **Reimers, Jan N.**  
21523-122 Sreet,  
Maple Ridge, British Columbia, V2x 3N7 (CA)  
Inventor : **Fuller, Eric Wayne**  
20493 Deniza Avenue  
Maple Ridge, B.C. V2X 8T7 (CA)

(74) Representative : **Silverman, Warren et al**  
**HASELTINE LAKE & CO.**  
Hazlitt House  
28 Southampton Buildings  
Chancery Lane  
London WC2A 1AT (GB)

(54) Novel method for preparing solid solution materials for secondary non-aqueous batteries.

(57) Lithiated manganese oxides are synthesized using a novel two stage process. Using appropriate starting materials, lithiation is accomplished via low temperature ion exchange in aqueous warm salt solution. A heating stage follows which completes the synthesis. Materials suitable for use as cathodes in lithium ion rechargeable batteries have been prepared in this way. Novel materials might also be prepared using a similar low temperature ion exchange process.

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Jouve, 18, rue Saint-Denis, 75001 PARIS

This invention relates to solid solution oxides, especially lithiated manganese oxides, processes for synthesizing these materials, and their use as active electrode materials in electrochemical cells. In particular, the invention relates to the synthesis of such materials for use as cathodes in lithium ion rechargeable batteries.

Lithium batteries are becoming increasingly popular in the market place as they offer advantages of high voltage and energy density over conventional aqueous technologies. Recent developments in the field are allowing lithium battery technologies to meet the demands of ever greater energy density requirements for electronics applications.

Primary lithium batteries and historically secondary lithium batteries have used metallic lithium or a lithium alloy for the anode and often a transition metal chalcogenide for the corresponding cathode. The discharge process of batteries constructed in this way involves the transfer of lithium atoms from the anode into the host cathode. Thus, primary cells preferably have minimal lithium in the cathode as fabricated in order to obtain maximum capacity on discharge. Certain advantages however can be obtained by partially lithiating the cathode prior to battery fabrication. Common commercial cathode materials include manganese oxide compounds. As taught in the Hitachi Maxell KK, Japanese patent publication 59-31182 (1984), discharge performance and shelf stability of a non-aqueous  $\text{LiMnO}_2$  primary cell can be improved by partial lithiation of the  $\text{MnO}_2$  cathode followed by appropriate heat treatment. This was accomplished by soaking the  $\text{MnO}_2$  in  $\text{LiOH}$  solution and then heat treating preferably around  $300^\circ\text{C}$ . The  $\text{MnO}_2$  contains significant amounts of bound water which is driven off by heating. In this publication, it is stated that the presence of lithium in the host  $\text{MnO}_2$  prevents undesirable changes on heating.

The prior art contains other references teaching similar ways of lithiating manganese oxides for use in batteries. Sanyo, Japanese Kokai 62-108455 (1987) disclose a secondary battery employing cathode of lithium doped gamma phase electrolytic manganese dioxide made in the same general way described in the Hitachi '182 publication. Toshiba, Japanese Kokai 62-126556 (1987) describe batteries made with cathode material prepared from  $\text{LiOH}$  treated  $\text{MnO}_2$ . Moli, U.S. patent 4,959,282, describe the preparation of what was called "X-phase" cathode material for batteries where the lithiated manganese oxide is first coated with  $\text{LiOH}$  solid via evaporation from solution followed by a heat treatment step. In all the preceding examples, only partial lithiation of the manganese compound is performed.

Recent developments in the field have led to the commercialization of rechargeable lithium batteries where a host compound, usually a form of carbon, has been used in place of lithium metal and/or alloy as the anode. During use of the battery, lithium ions are shuttled or rocked from the cathode to the anode on charge and from the anode to the cathode on discharge. Such batteries are called Lithium ion cells (T.Nagaura and K.Tozawa, Progress in Batteries and Solar Cells, 9, 209, (1990)) or Rocking Chair cells (J.R.Dahn, et al., J.Electrochem. Soc. 138, 2207 (1991)) Such batteries provide increased safety and cycle life over historical rechargeable lithium technologies.

It is desirable for practical reasons that the battery components be relatively stable in dry air for manufacturing purposes. It is also desirable that substantial amounts of lithium be incorporated in the electrode materials such that use of the inherent capacity of the materials can be maximized without having to add lithium in some other form. Lithium atoms therefore usually reside in the transition metal chalcogenide cathode when fabricated as the preferred compounds for use can incorporate large amounts of lithium yet still remain stable in dry air.

Sony Energy Tec Inc. was the first company to commercialize lithium ion batteries where  $\text{LiCoO}_2$  was used as a cathode material. Many other such materials have been proposed such as  $\text{LiNiO}_2$  (Goodenough et al., U.S.P. No. 4,302,518 and/or Dahn et al., J.Electrochem. Soc. 138, 2207, (1991))  $\text{LiMn}_2\text{O}_4$  (Ohzuku et al., J.Electrochem. Soc. 137, 769, (1990)) and  $\text{Li}_2\text{Mn}_2\text{O}_4$  (Tarascon et al., J. Electrochem. 138, 2864 (1991)).  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  adopt a layered structure of space group R-3m.  $\text{LiMn}_2\text{O}_4$  adopts the  $\text{AB}_2\text{O}_4$  spinel structure with space group Fd3m.  $\text{Li}_2\text{Mn}_2\text{O}_4$  as described in Tarascon et al., J. Electrochem. 138, 2864 (1991) is related to  $\text{LiMn}_2\text{O}_4$  in structure, but it is not believed to be entirely air stable. It is our belief that said  $\text{LiMn}_2\text{O}_4$  is hence not useful as a practical cathode material for Lithium ion batteries.

Each of these cathode materials can reversibly react with a certain amount of lithium between reasonable cutoff voltages that might be used in a practical Lithium-ion cell. These cutoff voltages are most likely about 2.5V and about 4.2V versus metallic Li. The specific capacities of  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$  between these voltage limits are about 140 mAh/g (J.N. Reimers and J.R. Dahn, J. Electrochem. Soc. 139, 2091 (1992)), 170 mAh/g, (J.R. Dahn, U. von Sacken and C.A. Michael, Solid State Ionics 44, 87 (1990)), and 110 mAh/g (T. Ohzuku, M. Kitagawa and T. Hirai, J. Electrochem. Soc. 137, 769, (1990)).

Recently, Ohzuku et al, Chemistry Express, 7, 193 (1992), discovered a new type of  $\text{LiMnO}_2$  prepared from  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\gamma\text{-MnOOH}$  at low temperature. Ohzuku et al. mixed stoichiometric amounts of the above reactants and then pressed them into a pellet. Different pellets were then heated in flowing nitrogen for several hours at temperatures between  $300^\circ\text{C}$  and  $1000^\circ\text{C}$  to prepare a series of materials. For materials prepared at

1000°C, the powder diffraction pattern resembled that of orthorhombic  $\text{LiMnO}_2$ , (Dittrich and Hoppe, Z. Anorg. Allg. Chemie 368, 262 (1969)). At lower temperature, (eg. 450°C) the patterns were different, consisting of Bragg peaks that could be assigned to  $\text{LiMnO}_2$  (of which some were very broad) and other peaks from an impurity phase. Nevertheless, Ohzuku et al. showed that material prepared at moderate temperature (between 300°C and 450°C apparently) reversibly reacted with about 190 mAh/gram of lithium between 2.0 and 4.25 V when operated as a lithium-ion cell cathode would be. In this application we call the material prepared at temperatures below 450°C, (excluding the impurity phase) Low Temperature  $\text{LiMnO}_2$  or LT- $\text{LiMnO}_2$ .

Cobalt and nickel are both much more expensive than manganese. For this reason, it is very important to use manganese-based materials in a price sensitive battery product provided performance penalties compared to cobalt and nickel are not overly severe. The new material reported by Ohzuku et al. apparently represents a major improvement in specific capacity compared to  $\text{LiMn}_2\text{O}_4$ . However,  $\text{LiMn}_2\text{O}_4$  delivers useable capacity at a higher voltage than LT- $\text{LiMnO}_2$ . Thus both materials appear very attractive for use as lithium ion battery cathodes.

Low cost, simple synthesis methods for such manganese based compounds are therefore desirable. Acta Chemica Sinica, Vol 39, No. 8, page 711-716 discusses an ion exchange material,  $\text{LiMn}_2\text{O}_4$ , resulting from treatment of electrolytic  $\text{MnO}_2$  in  $\text{LiOH}$  solution followed by a heating stage. The preparation of  $\text{LiMn}_2\text{O}_4$  is also disclosed in U.S. Patent No. 4,246,253 using a method involving sintering lithium carbonate and manganese dioxide at temperatures of 800°-900°C. It was shown in U.S. Patent No. 4,828,834 that a preferred  $\text{LiMn}_2\text{O}_4$  compound for use in rechargeable batteries could be prepared by reacting manganese dioxide with  $\text{Li}_2\text{CO}_3$  at 400°C or with  $\text{LiI}$  at 300°C in nitrogen. Ohzuku et al. proposed a method for preparing LT- $\text{LiMnO}_2$  which involves pelletizing an intimate mixture containing  $\text{LiOH} \cdot \text{H}_2\text{O}$  and heat treating. In all these cases, manganese compounds with substantial amounts of lithium were prepared. However in all cases, an intimate mixture of lithium salt and manganese oxide must be created prior to heat treatment. The actual incorporation of lithium by ion exchange into the manganese oxide disclosed in Acta Chemica Sinica is believed to be low since there are few atoms to exchange with. However, after evaporating away water from  $\text{LiOH}$  solution, a solid intimate mix of  $\text{LiOH}$  coated, partially exchanged manganese oxide would be obtained.

There are several possible problems with synthesis methods employing such solid state reactions of intimate mixes of solids. In order to make uniformly lithiated material it is important that the stoichiometry throughout is constant. A uniform reaction relies on the correct ratios of reactants being present on a local, small scale. Thus, uniformity of the reactant mix must be achieved on a very small scale. Purity problems can arise if the manganese compound is inadequately lithiated prior to heating fully, resulting in the formation of an undesired compound. Unreacted lithium salt can remain as an impurity. In some instances, the preferred Li salt reactant may be  $\text{LiOH}$ . However, this can readily convert to  $\text{Li}_2\text{CO}_3$  in air. Thus exposure of the mixture to the normal atmosphere prior to finishing heat treatment may be undesirable. A method of dealing with this particular problem is disclosed in Japanese Kokai 04-115459, wherein  $\text{Li}_2\text{CO}_3$  is converted to  $\text{LiOH}$  by introducing water vapour into the process air stream.

A method for preparing a solid solution of the form  $\text{A}_x\text{B}_y\text{MO}_z$  wherein A and B represent elements that can be exchanged as ions, and x is a number in the range from zero to about or equal to 2, y is a number in the range from greater than zero to about or equal to 2, and z is a number in the range from about or equal to 1.5 to about or equal to 3, and M is a transition metal, has now been found. The method comprises the steps of (a) selecting a starting solid solution having a desired molecular framework of the formula  $\text{A}_y\text{MO}_z$ , and an anionic compound of B wherein y' and z' have the same ranges as defined above for y and z respectively, but need not necessarily be the same numbers; and (b) conducting a controlled low temperature ion exchange on the starting solid solution, to a controlled extent, wherein the element A is replaced with the element B, to produce an at least partial ion exchanged solid solution of the form  $\text{A}_x\text{B}_y\text{MO}_z$ .

Elements that can be exchanged as ions include alkali and alkaline earth metals. Typical exchangeable elements that may find utility include those selected from H, Li, Na, K, Cs, Ca, Mg and Rb and mixtures thereof. M can be a transition metal element selected from the group consisting of Mn, Fe, Ni, Co, V, Cr and Sc.

The solid solution prepared by the method of the invention can be subsequently heated to complete the synthesis of a desired material.

The controlled ion exchange aspect of the method of the invention can be conducted in an aqueous medium.

Additionally, a primary or rechargeable battery can be manufactured wherein at least a portion of one electrode comprises a solid solution material prepared according to the method of the invention. In particular, the inventors have discovered that  $\text{LiMn}_2\text{O}_4$  and LT- $\text{LiMnO}_2$  can be prepared in appreciably pure form using a simple two stage process embodying the invention. The first stage of the process, the lithiation stage, is accomplished via low temperature ion exchange in aqueous warm salt solution. The second stage involves a heat treatment step for the removal of hydrogen as water and/or for structural rearrangement. A key to such process

is the use of a suitable starting material with the proper initial structure and sufficient inserted ion already present such that it can be exchanged with the total amount of lithium desired in the final compound. The other key is that the exchange process requires a solvent, in this case water. Thus no intimate mix of solid Li salt and manganese compound is required as an intermediary step with its corresponding drawbacks. Since other chemically similar starting materials are known to exist, the inventors expect that this method will be applicable to the synthesis of other solid solution materials, especially other Li manganese oxide phases, of interest for use in batteries as well.

Specifically, both  $\text{LT-LiMnO}_2$  and  $\text{LiMn}_2\text{O}_4$  have been synthesized using this novel process and using  $\gamma\text{-MnOOH}$  as the starting material. Lithiation was accomplished by boiling solid  $\gamma\text{-MnOOH}$  particles in sufficient 4M LiOH solution. During the boiling, an ion exchange reaction occurs:



The initial molarity and volume of the LiOH solution which is added per unit mass of  $\gamma\text{-MnOOH}$  can be used to adjust the extent of lithiation and to minimize the amount of LiOH which remains in the solution after reaction. Predominantly complete ion exchange is possible. After sufficient time, the suspended  $\text{LT-Li}_x\text{H}_{1-x}\text{MnO}_2$  particles are recovered from the solution by filtering or settling or centrifugation. The material can then either be rinsed with pure  $\text{H}_2\text{O}$  to remove excess LiOH, if any, or left unrinsed. Some reverse ion exchange can occur if rinsing is used. This can be used to adjust the extent of lithiation if desired. The powder is then dried by heating at temperatures between  $100^\circ\text{C}$  and  $350^\circ\text{C}$  in either vacuum or inert gas. Heating above  $350^\circ\text{C}$  may be used if structural rearrangement is desired. This represents a substantial simplification compared to the method of Ohzuku et al. in the preparation of  $\text{LT-LiMnO}_2$ .

In the preparation of  $\text{LT-LiMnO}_2$ , it is thought to be important that the ion exchange reactions be completed at temperatures below about  $220^\circ\text{C}$ . The reason is that  $\gamma\text{-MnOOH}$  decomposes above this temperature to form  $\text{Mn}_2\text{O}_3$  and water. For rapid ion exchange reactions, involving the  $\gamma\text{-MnOOH}$  framework, it is essential that this framework not be destroyed. Therefore it is most desirable to perform these ion exchange reactions below about  $220^\circ\text{C}$ .

Lithium/ $\text{LT-LiMnO}_2$  test cells constructed with such materials give reversible capacities between 2.5 and 4.2 V of more than 170 mAh/g. Once the powders are heated to  $450^\circ\text{C}$  or above, the reversible cell capacity drops dramatically (to about 60 mAh/g for material heated at  $450^\circ\text{C}$ ). This reduction coincides with changes to the x-ray diffraction profile of the material with heating. Between  $350^\circ\text{C}$  and  $450^\circ\text{C}$ , the crystallinity of  $\text{LT-LiMnO}_2$  improves dramatically, apparently reducing the reversible capacity.

In the description which follows, reference will be made to the following examples, wherein:

Figure 1 shows a preferred construction of a rechargeable lithium ion battery incorporating a cathode material prepared using the invention process.

Figure 2 shows the construction of the laboratory test cell employed to illustrate the electrochemical behaviour of example materials.

Figure 3 shows the powder X-ray diffraction pattern of  $\text{LT-LiMnO}_2$  prepared in comparative example 1.

Figure 4 shows the voltage versus capacity curves for a laboratory test cell using a lithium anode and a cathode of the material prepared in comparative example 1.

Figure 5 shows the voltage versus capacity curve for a laboratory test cell using a lithium anode and a cathode of the material used in comparative example 2 plus the curve of figure 4 for comparison.

Figure 6 shows the powder X-ray diffraction pattern of  $\text{LT-LiMnO}_2$  prepared in invention example 1.

Figure 7 shows the voltage versus capacity curves for a laboratory test cell using a lithium anode and a cathode of the material prepared in invention example 1.

Figure 8 shows the powder X-ray diffraction pattern of  $\text{LT-Li}_x\text{MnO}_2$  prepared in invention example 2.

Figure 9 shows the voltage versus capacity curves for a laboratory test cell using a lithium anode and a cathode of the material prepared in invention example 2.

Figure 10 shows the powder X-ray diffraction pattern of  $\text{LiMn}_2\text{O}_4$  prepared in invention example 3.

Figure 11 shows the thermogravimetric data for foil wrapped pellets tested at different heating rates in illustrative example 1.

Figure 12 shows the thermogravimetric data for foil wrapped pellets prepared with anhydrous LiOH or  $\text{LiOH.H}_2\text{O}$  in illustrative example 1.

Figure 13 shows the thermogravimetric data for  $\gamma\text{-MnOOH}$  by itself as tested in illustrative example 1.

Figure 14 shows the powder X-ray diffraction pattern of  $\text{LT-Li}_x\text{MnO}_2$  prepared in illustrative example 2.

Figure 15 shows the voltage versus capacity curves for a laboratory test cell using a lithium anode and a cathode of the material prepared in illustrative example 2.

Figure 16 shows the thermogravimetric data for the material prepared as in illustrative example 3.

Figure 17 shows the powder X-ray diffraction pattern of the mixture of phases prepared in illustrative example 4.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 2689

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
X	MATERIALS RESEARCH BULLETIN., vol. 17, 1982, OXFORD GB pages 117 - 123 CLAUDE DELMAS ET AL 'A NEW VARIETY OF LiCoO <sub>2</sub> WITH UNUSUAL OXYGEN PACKING OBTAINED BY EXCHANGE REACTION' * page 118 *	1-4	C01G1/02 C01G45/00 H01M4/50 C01G51/00
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 407 (E-675) 27 October 1988 & JP-A-63 148 550 (SANYO ELECTRIC CO) 21 June 1988 * abstract *	1-5, 7, 9	
X	PATENT ABSTRACTS OF JAPAN vol. 5, no. 137 (E-072) 29 August 1981 & JP-A-56 073 864 (MATSUSHITA ELECTRIC IND) 18 June 1981 * abstract *	1-12	
A	GB-A-2 087 858 (KOICHI MIZUSHIMA) * the whole document *	1-5	<div>TECHNICAL FIELDS SEARCHED (Int. Cl. 5)</div> <div>C01G H01M</div>
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>22 August 1994</b>	Examiner <b>LIBBERECHT, E</b>
<div>CATEGORY OF CITED DOCUMENTS</div> <div> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons Δ : member of the same patent family, corresponding document</p> </div>			

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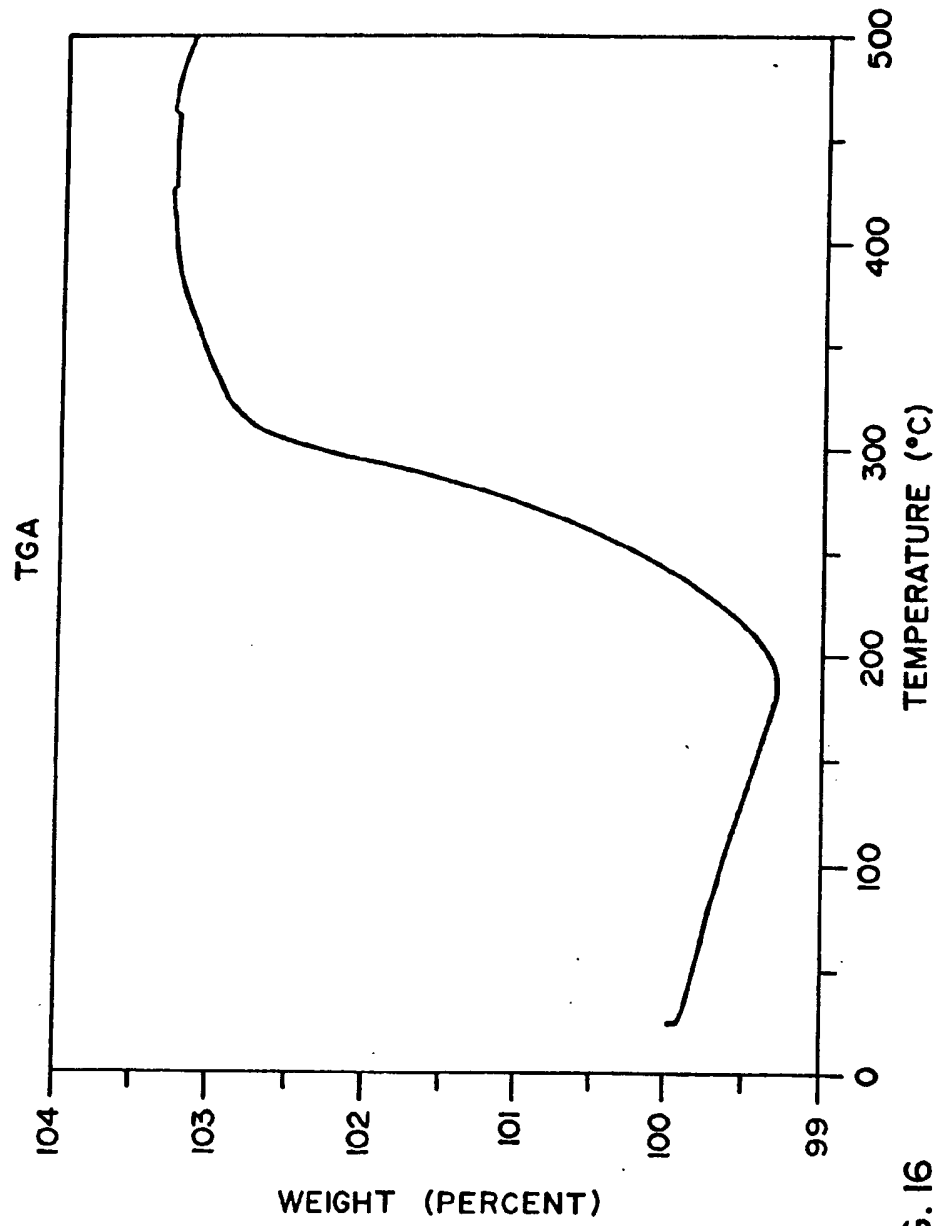


FIG. 16

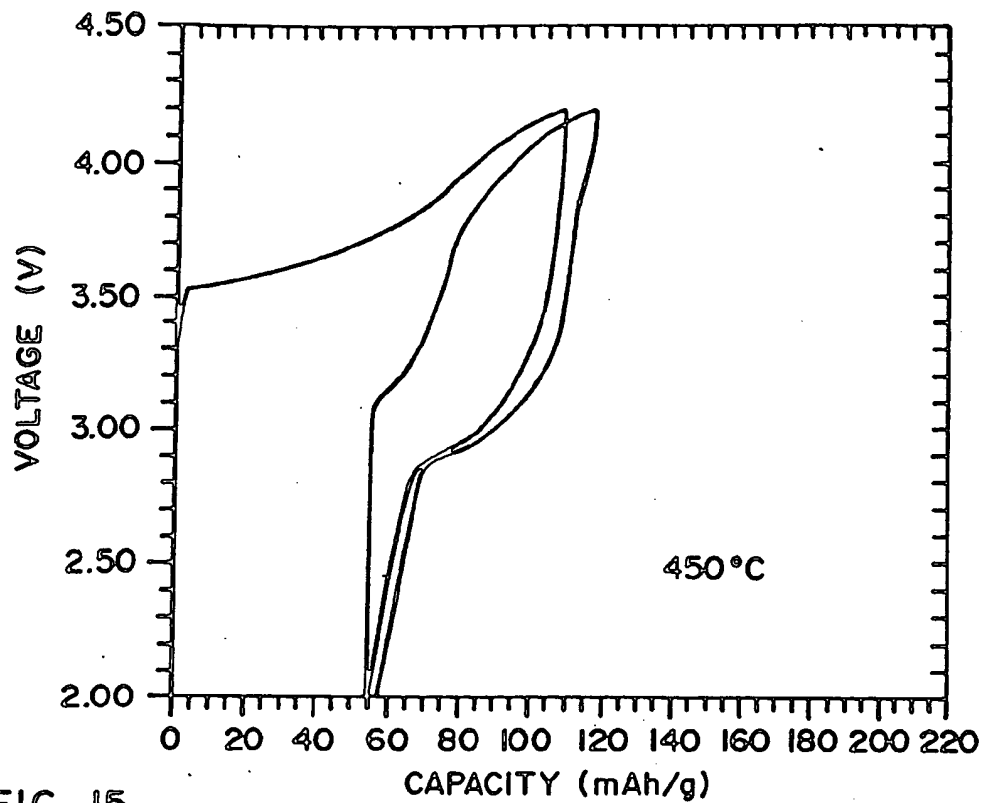


FIG. 15

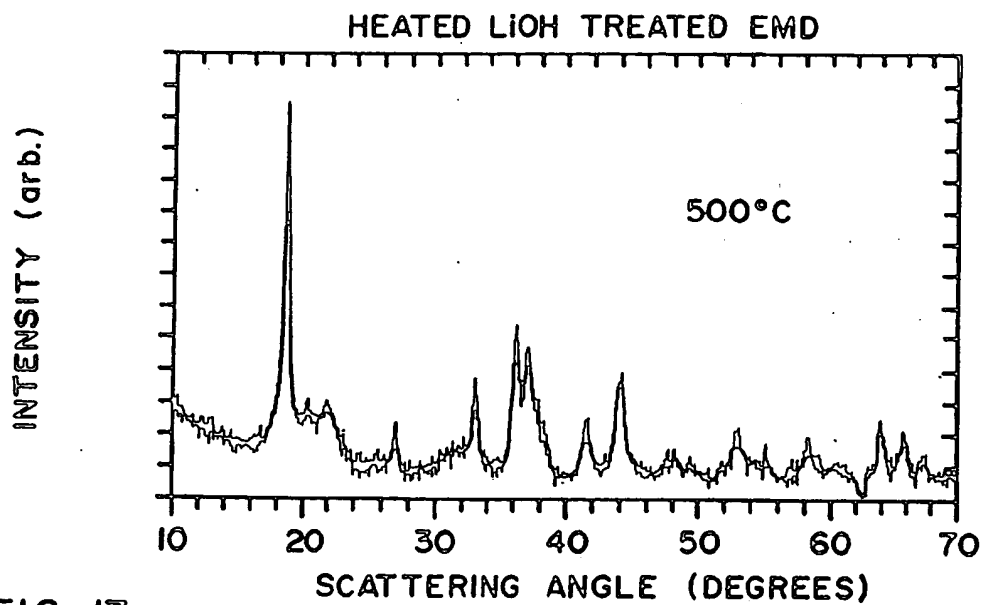


FIG. 17

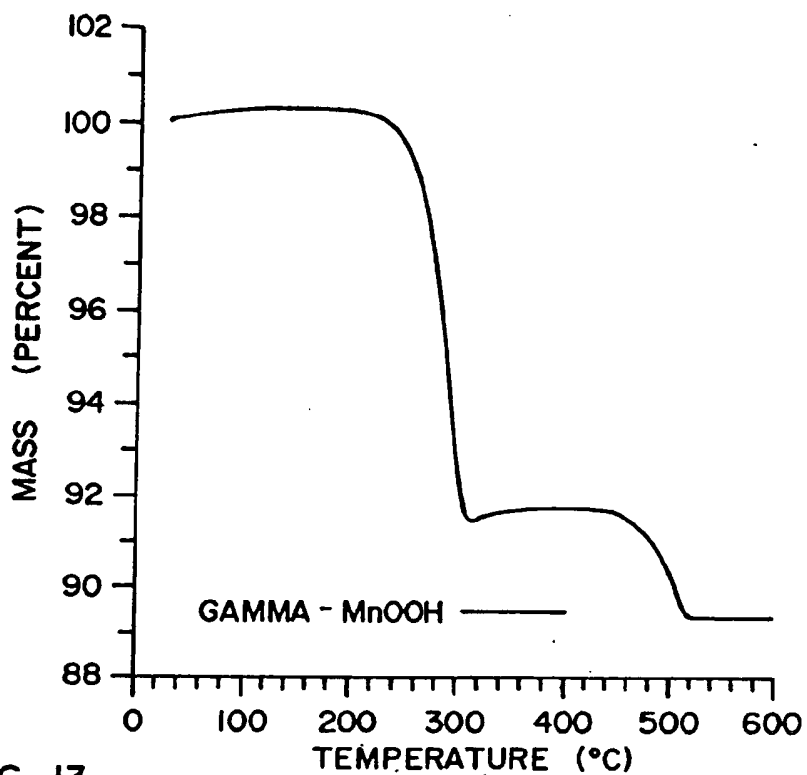


FIG. 13

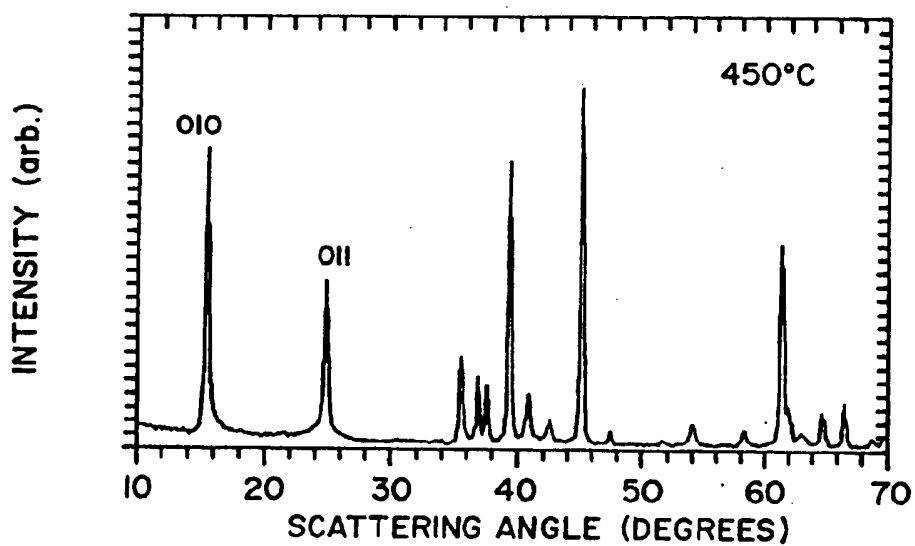


FIG. 14



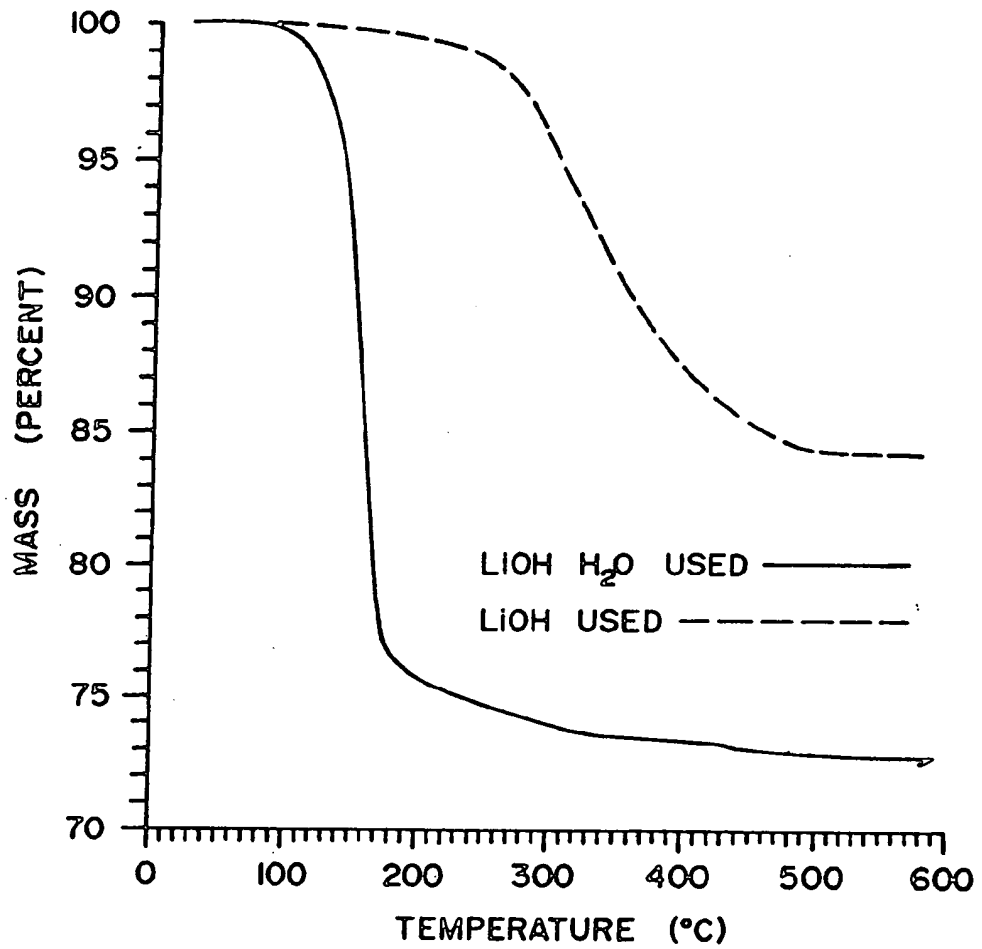


FIG. 12

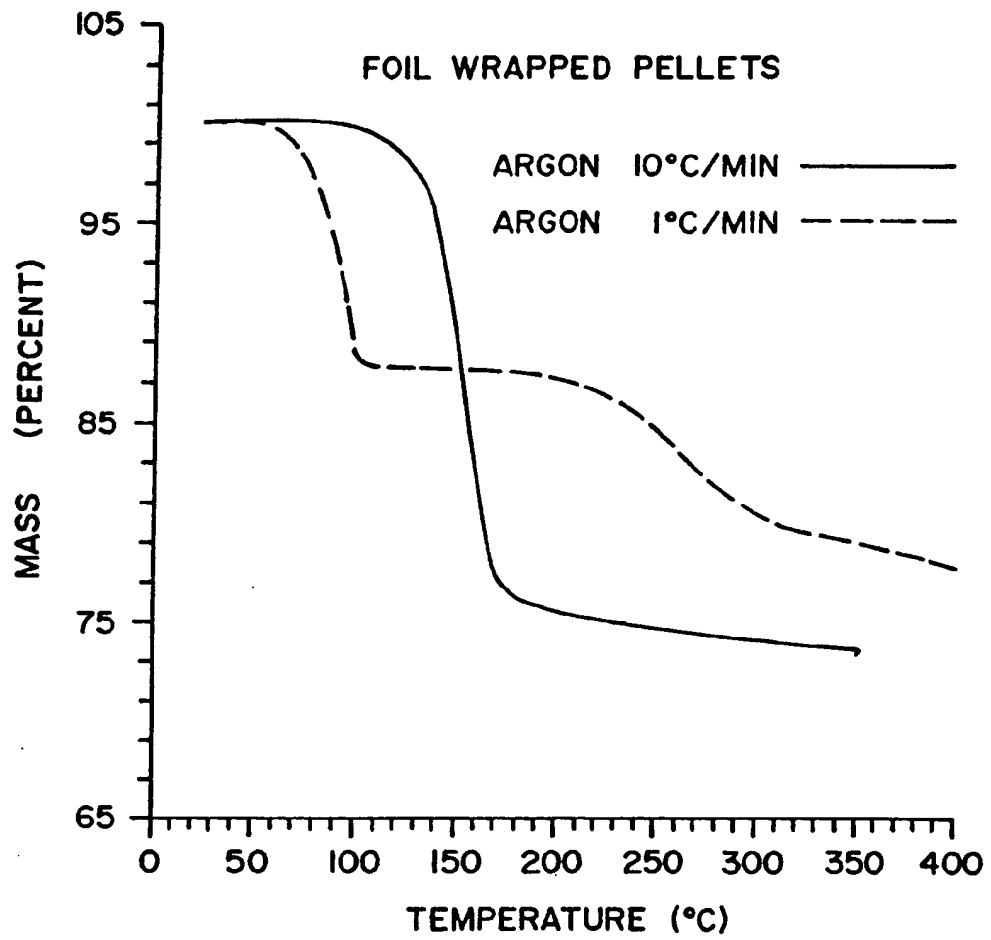


FIG. II

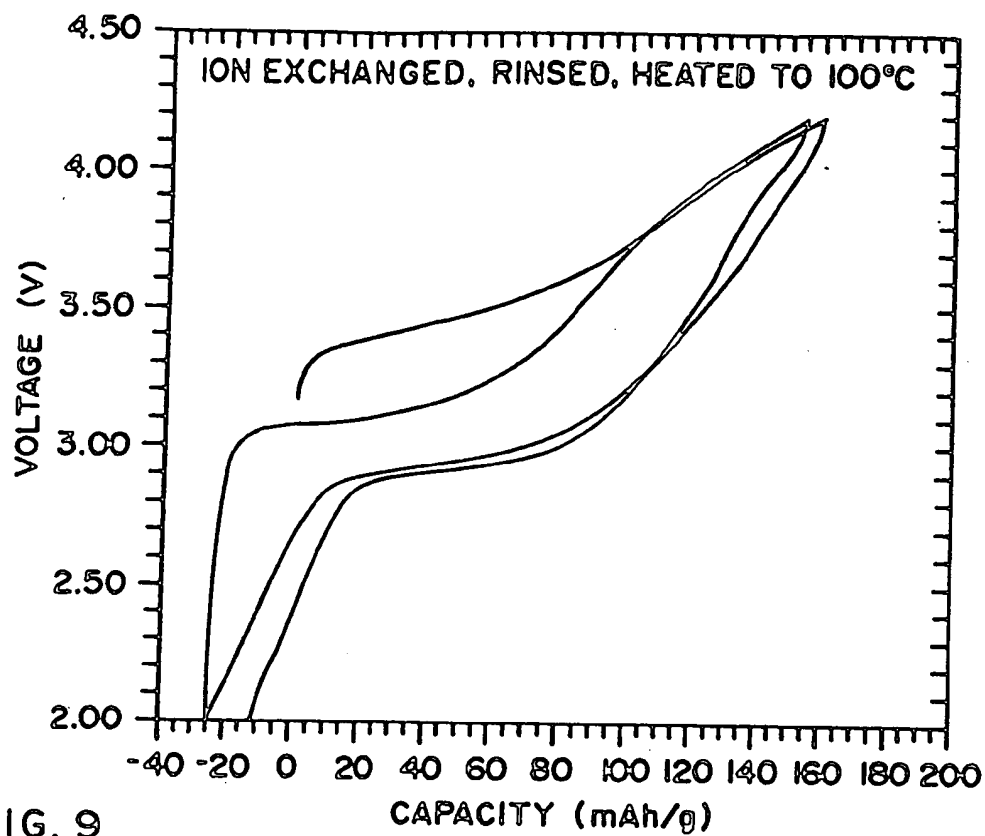


FIG. 9

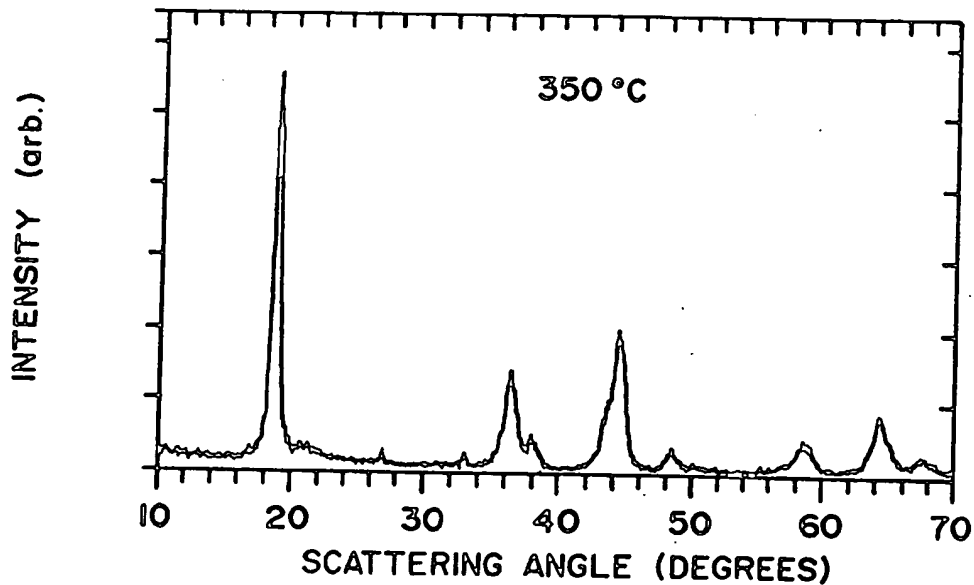


FIG. 10

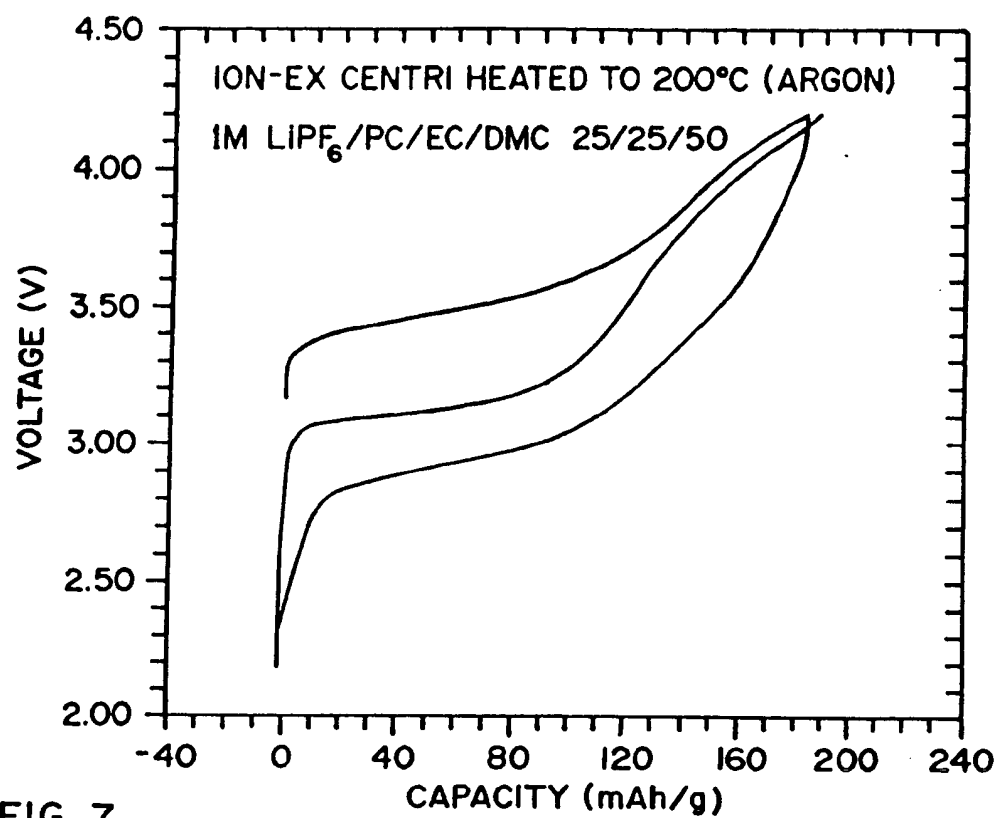


FIG. 7

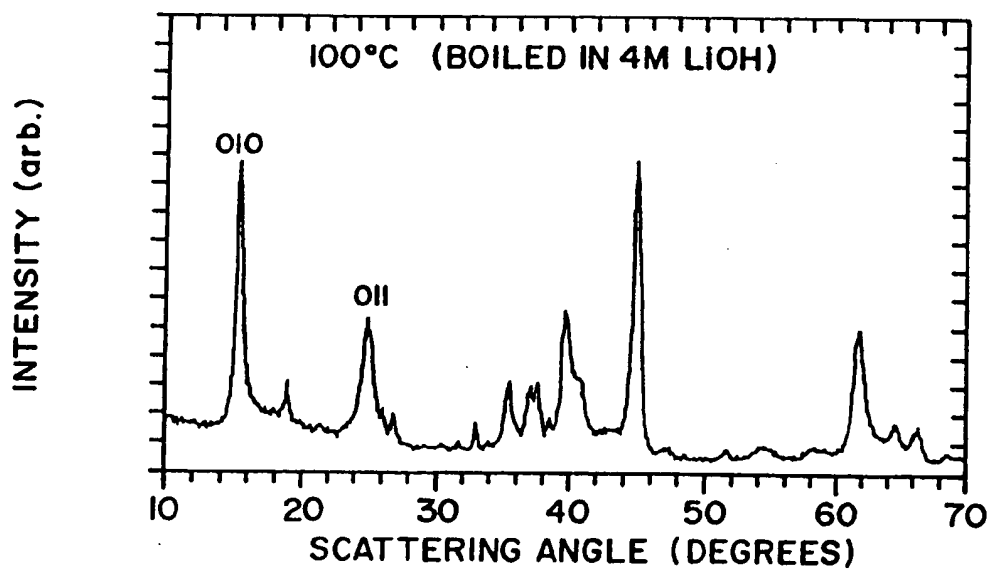


FIG. 8

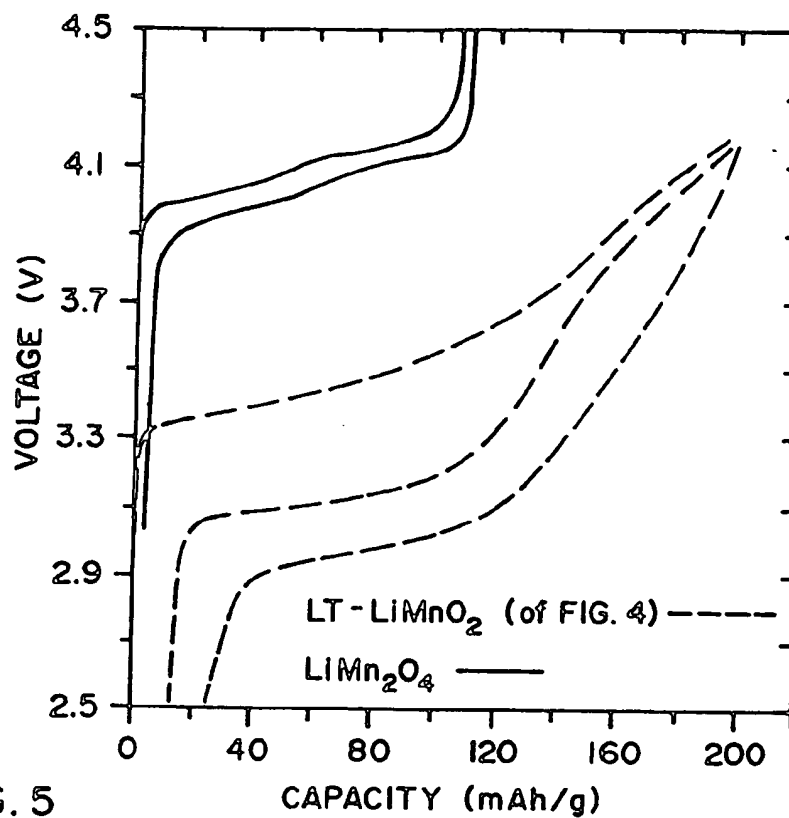


FIG. 5

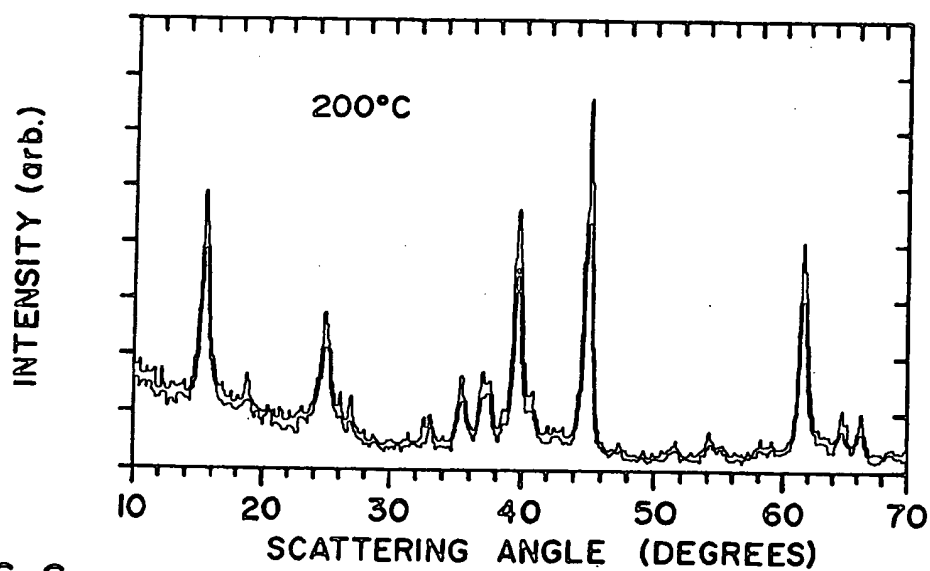


FIG. 6

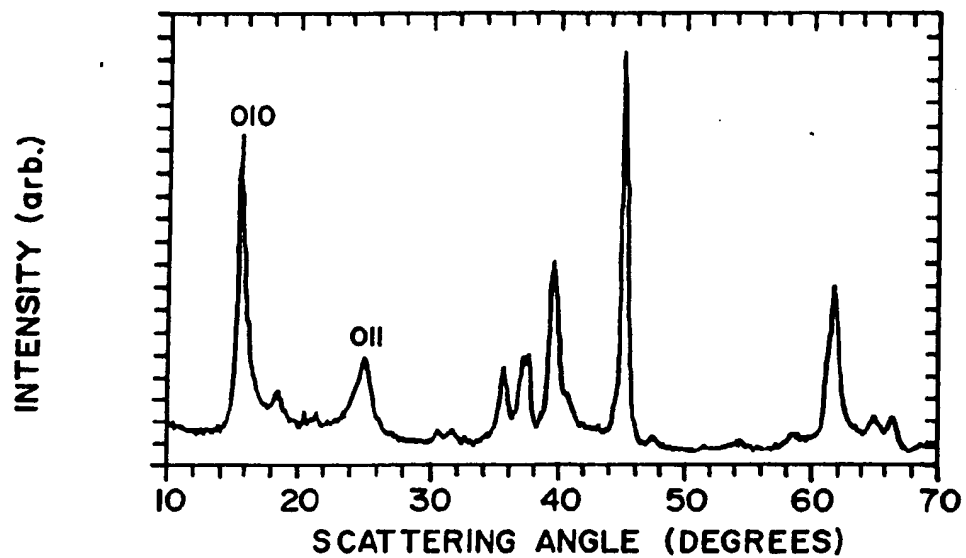


FIG. 3

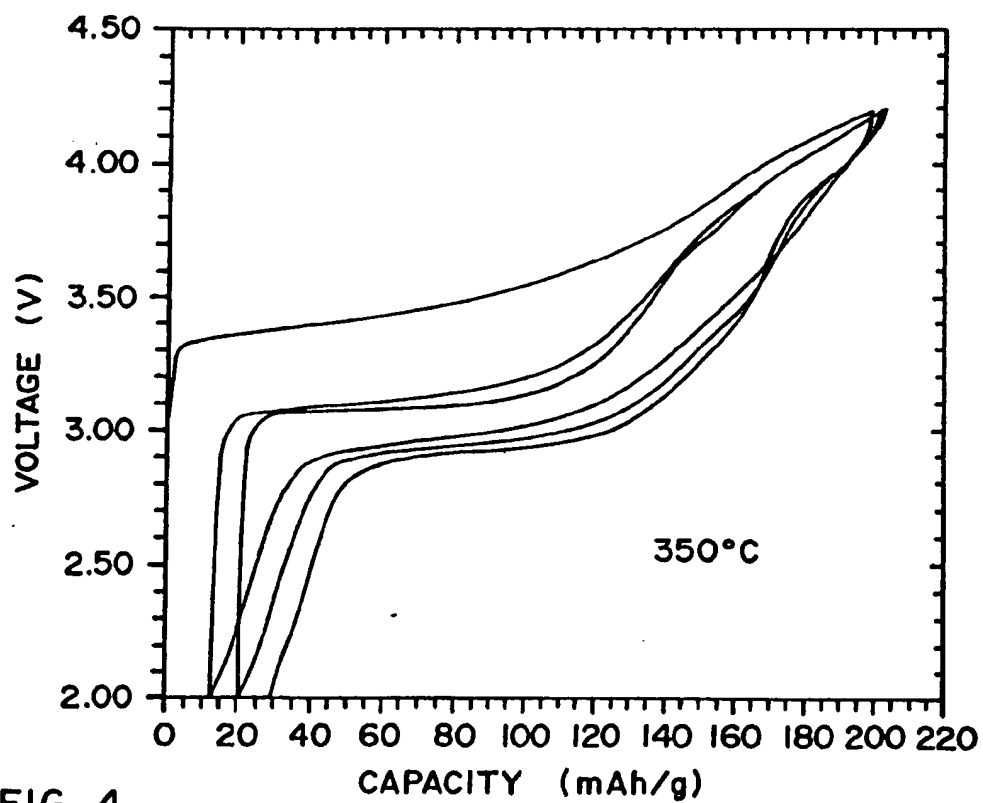
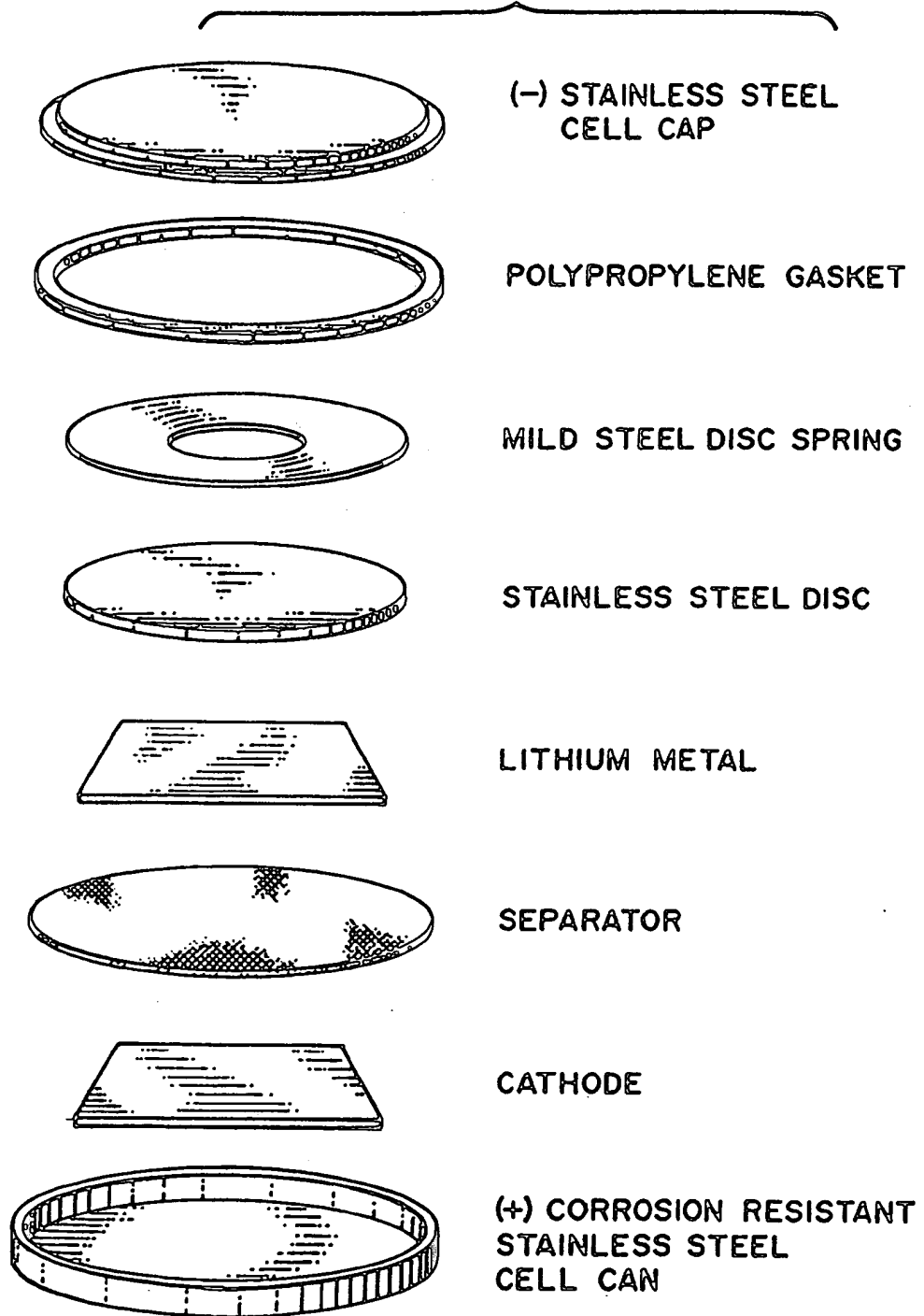


FIG. 4

FIG. 2



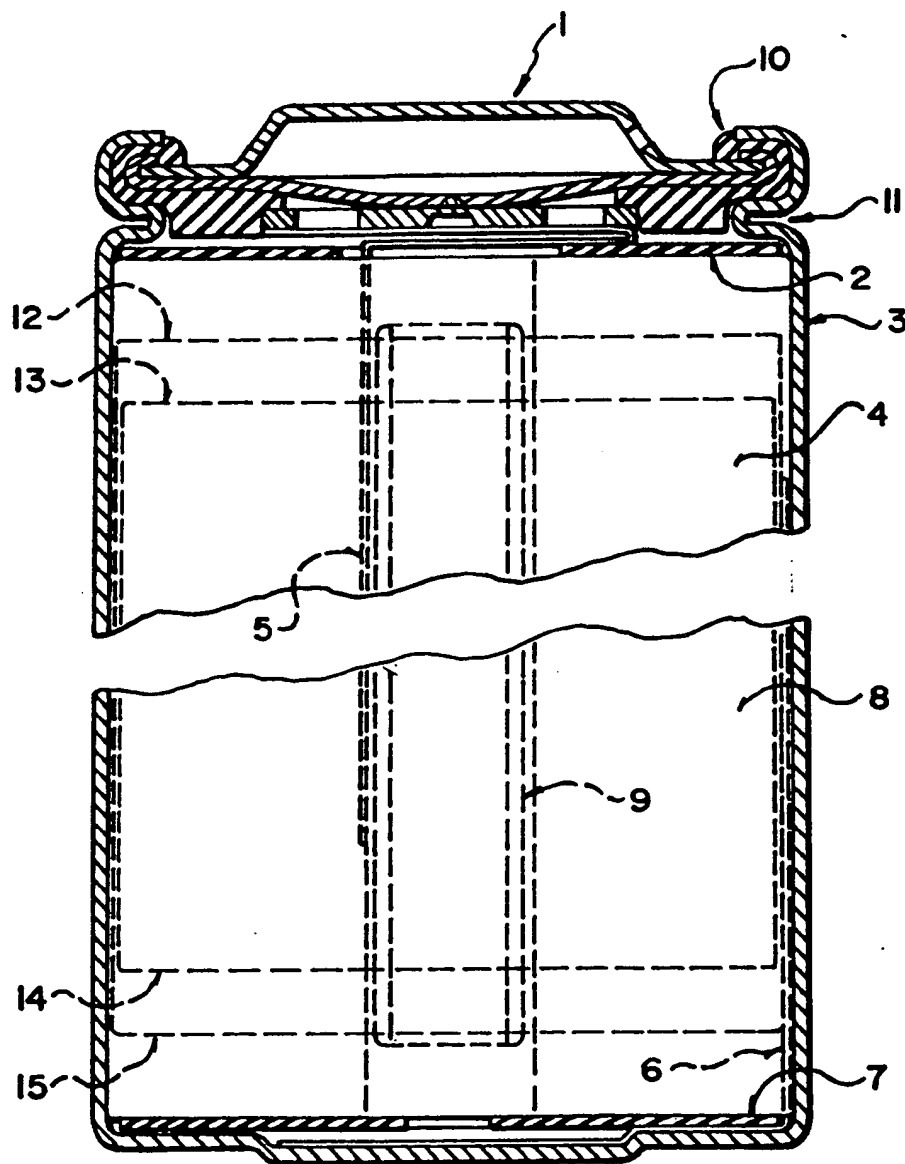


FIG. 1



zero to about or equal to 2, y is a number in the range from greater than zero to about or equal to 2, and z is a number in the range from about or equal to 1.5 to about or equal to 3, and M is a transition element, which comprises:

- (a) selecting a starting solid solution having a desired molecular framework of the formula:  $A_yMO_z$ , and an anionic compound of B, wherein A and B are as defined above and y' and z' have the same ranges as defined above for y and z, but need not necessarily be the same numbers; and
  - (b) conducting a controlled low temperature ion exchange on the starting solid solution, to a controlled extent, wherein the element A is replaced with the element B, wherein A and B are as defined above, to produce an at least partial ion exchanged solid solution of the form  $A_xB_yMO_z$ .
2. A method as claimed in claim 1, wherein A and B represent elements selected from H, alkali metals especially Li, Na, K, Cs, and Rb and alkaline earth metals, especially Mg and Ca.
  3. A method as claimed in claim 2, wherein the transition metal is one capable of forming a compound representable by the molecular formula  $HMO_2$  or  $H_2MO_2$ .
  4. A method as claimed in claim 3, wherein M is selected from Mn, Fe, Ni, Co, V, Cr and Sc and mixtures of two or more thereof.
  5. A method as claimed in any preceding claim 1 wherein the ion exchanged solid solution of  $A_xB_yMO_z$  is heated to complete synthesis.
  6. A method as claimed in any preceding claim, wherein the controlled ion exchange is conducted in an aqueous medium.
  7. A method as claimed in any preceding claim, wherein the compound  $A_yMO_z$  in the starting solid solution is selected from the group consisting of  $\alpha$ - $MnOOH$ ,  $\beta$ - $MnOOH$ ,  $\gamma$ - $MnOOH$  and  $Mn(OH)_2$ , and mixtures thereof.
  8. A method as claimed in any preceding claim, wherein the ion exchange is conducted at a temperature between about 0°C and about 300°C.
  9. A method as claimed in claim 7, wherein B is lithium.
  10. A method as claimed in any preceding claim, wherein a solid solution of the formula  $Li_yMnO_z$ , wherein y and z are as defined in claim 1, is prepared from the stances  $LiOH$  and  $\gamma$ - $MnOOH$ .
  11. A method as claimed in claims 1 to 3 of synthesizing a lithiated manganese oxide of the form  $Li_yMnO_z$ , wherein y is a number of a range greater than zero and less than or equal to 1, and z is a number of about 2 which comprises:
    - (a) selecting an ionic compound of Li to be used for purposes of ion exchange;
    - (b) conducting a controlled aqueous ion exchange at a temperature below 300°C on  $\gamma$ - $MnOOH$  where H is replaced by Li to a controlled extent to produce an ion exchanged compound  $H_xLi_yMnO_z$  wherein x is a number of a range greater than or equal to zero and less than or equal to 1; and
    - (c) heating the ion exchanged compound to complete the synthesis.
  12. A primary or rechargeable battery wherein at least a portion of one electrode comprises a solid solution material prepared according to the method of any preceding claim.

TABLE 3

Transition Metal Oxide Hydrides MOOH and M(OH) <sub>2</sub> Minerals							
Structure	Sc	V	Cr	Mn	Fe	Co	Ni
Ramsdellite Orth. P6mm	$\alpha$ -ScOOH	Montroselite	Bracewellite, Orth. P6mm	Grondite $\alpha$ -MnOOH	Goethite $\alpha$ -FeOOH	No Name	
LiMnO <sub>2</sub> Str. Hex. R-3m 3R Stacking			Grimaldite -3R			Heterogenite -3R	
Hex. P6 <sub>3</sub> /mmc 2H stacking					Ferrosylvite *	Heterogenite -2H	
Hex. P3 <sub>2</sub> 12 1H Stacking				Pyrochroite Mn(OH) <sub>2</sub>	$\delta$ -FeOOH & Fe(OH) <sub>2</sub>	$\beta$ -Co(OH) <sub>2</sub>	$\beta$ -NiOOH ** & Theophanite Ni(OH) <sub>2</sub>
InOOH Str. Orth. P2 <sub>1</sub> mm	No Name (ScOOH)	No Name (VOOH)			No Name (FeOOH)		No Name (High Pres.)
Manganite Mono. P2 <sub>1</sub> /a				$\gamma$ -MnOOH*			
Lepidocrocite Orth. Amam	$\gamma$ -ScOOH				$\gamma$ -FeOOH Lepidocrocite		
Layered				Fairbridgeite $\beta$ -MnOOH			
Orth. Pmm			Cyanite				
Cryptomelane Struc. Tet. I4/m					Akaganeite		
Hex. 4or 5H stacking							$\gamma$ -NiOOH

\* distorted from ideal 2H-Heterogenite structure

\*\* based on only 3 diffraction lines

## Claims

1. A method of preparing a solid solution of the form



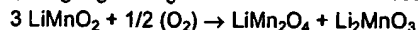
wherein A and B represent elements that can be exchanged as ions and x is a number in the range from

4,828,834 regarding  $\text{LiMn}_2\text{O}_4$ .

### Example 3:

5 3.543g  $\text{LiOH}\cdot\text{H}_2\text{O}$  and 6.457g  $\gamma\text{-MnOOH}$  were ground together to prepare an intimate mixture. From this mixture, 4.595g was extracted and pressed at 1000 bar into a 1" diameter pellet. The pellet was wrapped in Al foil and heated to 200°C for 1 hour in air. The final mass of the pellet was 3.334g after heating. For a 27.7% weight loss (expected if the product is  $\text{LT-LiMnO}_2$ ) the final mass is calculated to be 3.322g, in good agreement with experiment. The x-ray diffraction pattern of this powder resembled that shown in Figures 3,6 and 8, showing that  $\text{LT-LiMnO}_2$  was indeed produced.

10 A TGA analysis of a powdered sample of the material of invention example 2 was performed in an air atmosphere. As shown in Figure 16, weight gain begins near 200°C as the reaction



occurs. The weight gain expected in this reaction is 5.6%, but the experiment only shows about 3%, suggesting that it has not gone fully to completion, or that another reaction has taken place. The x-ray diffraction profile of the heated product does resemble that of  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_2\text{MnO}_3$ .

20 This example shows that once formed,  $\text{LT-LiMnO}_2$  is stable in air to just under 200°C. Above this temperature, a vacuum or inert gas such as Argon, must be used for processing. This demonstrates the importance of the type of process gas used and that simplification is possible if low temperature processing can be used.

### Example 4:

25 3.0 gms of electrolytic  $\text{MnO}_2$  or EMD (from Mitsui, TAD I grade) was refluxed under boiling conditions in 50 ml of 4M  $\text{LiOH}$  solution for six hours. Some of the suspension was poured into a centrifuge tube and settled by centrifugation. The liquid was then decanted, leaving minimal residual salt solution behind. The resultant wet powder was then heat treated in air at 500°C for greater than two hours. According to the Acta Chemica Sinica reference mentioned previously, these are the optimum conditions for preparing the ion exchange material identified as  $\text{LiMn}_2\text{O}_4$ . Figure 17 shows the x-ray diffraction pattern of the example material. It is clearly a mixture of phases which may include some contribution from  $\text{LiMn}_2\text{O}_4$ , but is far from substantially pure.

30 While EMD has some bound water, it does not have a substantial amount. Consequently, EMD is often represented as  $\text{MnO}_2$  only, without mention of hydrogen. Since virtually all the residual  $\text{LiOH}$  in solution was decanted away and since there is insufficient hydrogen to exchange with lithium in EMD, the material  $\text{LiMn}_2\text{O}_4$  was not the result of the example process. The Acta Chemica Sinica reference does not disclose sufficient detail but their result can easily be explained if significant residual  $\text{LiOH}$  remained prior to heat treatment (ie: an intermediary step wherein the partially exchanged lithium  $\text{MnO}_2$  compound is in intimate contact with  $\text{LiOH}$ ).

35 This example demonstrates that the invention process differs from the prior art and that  $\text{LiMn}_2\text{O}_4$ , a compound with substantial Li content, cannot be prepared by ion exchange if the starting material does not have a substantial amount of ions with which to exchange.

40 While the disclosure only shows some specific materials have been prepared using this novel process, it is intended that other materials prepared in a similar manner be within the scope of this invention. A table of starting materials that could be used to prepare useful and perhaps novel materials using this process is shown in the following.

45 Members of said Table include a variety of transition metal oxide hydroxides that can be represented as either  $\text{MOOH}$  or  $\text{M}(\text{OH})_2$ , or alternatively, as either  $\text{HMO}_2$  and  $\text{H}_2\text{MO}_2$  respectively, wherein M can be Mn, Fe, Ni, Co, V, Cr or Sc. The data for said Table has been compiled using information provided in the JCPDS-X-ray Powder Diffraction Database (1990). Some members have been synthesized artificially and have no given name. In like manner to the aforementioned examples, it is expected that H atoms in members of said Table might be exchanged for other elements via the method of the invention.

50

55

material.

### Example 3:

5 The material of inventive example 2 was further heated to 350°C in argon for 18 hours. The diffraction pattern for this material is given in Figure 10. This pattern no longer resembles that of the  $\text{LiMnO}_2$  phase prepared in comparative example 1 and inventive examples 1 and 2. Instead this pattern is close to that of  $\text{LiMn}_2\text{O}_4$  shown in comparative example 2. Thus it is presumably possible to prepare  $\text{LiMn}_2\text{O}_4$  and other Li-Mn-O compounds at low temperatures by preparing the "right"  $\text{Li}_x\text{H}_{1-x}\text{MnO}_2$  compound by controlled ion exchange followed by a suitable heat treatment.

### Illustrative Examples

#### Example 1:

15 6.554 g  $\gamma\text{-MnOOH}$  and 3.445 g  $\text{LiOH}\cdot\text{H}_2\text{O}$  were thoroughly mixed together using the automatic grinder. After mixing, about 0.1 gram of the mixture was pressed together at 1000 bar as in comparative example 1. Two small pieces of pellet (about 30 mg) were broken off and wrapped in a small piece of Al foil having known weight. The wrapped pieces were then subjected to TGA analysis at two different heating rates under flowing argon. One run was @ 1°C/min and the other was @ 10°C/min.

Next, Anhydrous  $\text{LiOH}$  and  $\gamma\text{-MnOOH}$  were mixed in a 1:1 stoichiometric ratio by grinding for 5 minutes. The mixture was pressed into a pellet at 1000 bar as before. A small piece of this pellet was wrapped in a known mass of aluminum foil and then subjected to TGA analysis under an argon atmosphere.

Figure 11 shows the weight loss versus temperature for both the TGA analyses on material prepared using  $\text{LiOH}\cdot\text{H}_2\text{O}$ . At 10°C/min heating rate, the reaction between  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\gamma\text{-MnOOH}$  occurs in a single event beginning just over 100°C in this analysis and ending near 170°C. The water of hydration of  $\text{LiOH}\cdot\text{H}_2\text{O}$  does not leave until over 100°C due to the foil wrapping. Thus there is water present to facilitate the ion exchange reaction to form  $\text{LT-LiMnO}_2$ . At 1°C/min heating rate, there is extensive weight loss before 100°C, as the water of hydration of  $\text{LiOH}\cdot\text{H}_2\text{O}$  is lost through the cracks in the foil wrapping since the time taken to reach 100°C is ten times longer. In T. Ohzuku et al., J. Electrochem. Soc. 137, 769, (1990), foil wrapping was not specified. This omission leads to early water loss at the exterior of the pellet and then to incomplete ion exchange at low temperature.

This phenomena is demonstrated further in comparing this to the results obtained with anhydrous  $\text{LiOH}$  and  $\gamma\text{-MnOOH}$  where the reaction doesn't begin until over 220°C. Figure 12 shows TGA analyses of the  $\text{LiOH}\cdot\text{H}_2\text{O}$  sample and anhydrous  $\text{LiOH}$  sample both heated at 10°C/min rate. At 220°C,  $\gamma\text{-MnOOH}$  begins to decompose as is shown on a similar TGA analysis on  $\gamma\text{-MnOOH}$  by itself in Figure 13. Neither the anhydrous  $\text{LiOH}$  sample nor the 1°C/min sample become  $\text{LT-LiMnO}_2$  after heating to 350°C, because insufficient water remains in the samples to facilitate the ion exchange between Li and H before the  $\gamma\text{-MnOOH}$  decomposes near 220°C. Note that the expected mass loss in the reaction  $\text{LiOH}\cdot\text{H}_2\text{O} + \gamma\text{-MnOOH} \rightarrow \text{LiMnO}_2$  is 27.7%, consistent with the sample heated at 10°C/min. To lower reaction temperatures as much as possible and to minimize such decomposition, water must be present as the ion-exchange solvent, so that  $\text{LiOH}$  is effectively in the solution phase.

This example shows that the presence of water is a key to the invention process and also to a prior art process.  $\text{LiMnO}_2$  clearly forms from a pressed pellet reaction below 200°C, if water vapour (in this case from the water of hydration of  $\text{LiOH}\cdot\text{H}_2\text{O}$ ) is present until about 100°C.

#### Example 2:

50 A wrapped pellet as in comparative example 1 was prepared and heated to 450°C under argon flow for 18 hours. The diffraction pattern of the powdered product is shown in Figure 14. This agrees well with the literature pattern described in comparative example one. Notice that the width of the 011 peak near 24.7 degrees has decreased compared to the data shown in Figure 3. This is due to increased crystallinity on higher temperature heating.

A  $\text{Li/LiMnO}_2$  cell was assembled using this powder. Figure 15 shows the voltage-capacity relation for this cell. This cell obtains only about 60 mAh/g of reversible capacity between 2.0 and 4.2 V.

This example illustrates that the electrochemical properties of this lithium manganese oxide can be drastically reduced by overheating to 450°C. The correlation of broader x-ray diffraction peaks with reduced heat treatment temperature to greater electrochemical capacity is similar in general to that mentioned in USP No.

TABLE 2  
LITERATURE DIFFRACTION PATTERN FOR  $\text{LiMn}_2\text{O}_4$

MILLER INDICES	SCATTERING ANGLE	RELATIVE INTENSITY
111	18.611	100
220	30.650	1
311	36.085	38
222	37.747	10
400	43.869	33
331	48.047	7
511	58.056	10
440	63.780	16
531	67.079	7

A  $\text{Li/LiMn}_2\text{O}_4$  test cell was prepared using  $\text{LiMn}_2\text{O}_4$  (from Cyprus-Foote Mineral Corp., Exton, PA., USA) and the methods described earlier. Figure 5 shows the voltage-capacity relation for this cell compared to that used for Figure 4. The data for the  $\text{LiMn}_2\text{O}_4$  cell are in good agreement with those in the literature (T. Ohzuku et al., J. Electrochem. Soc. **137**, 769, (1990)). This shows the capacity advantage of  $\text{LT-LiMnO}_2$  over  $\text{LiMn}_2\text{O}_4$ .

These two examples illustrate the electrochemical behaviour of  $\text{LT-LiMnO}_2$  and  $\text{LiMn}_2\text{O}_4$ , that prior art methods can be successfully duplicated, and that the laboratory cell assembly and testing techniques are sound.

#### Invention Examples

##### Example 1:

5.0 grams of  $\gamma\text{-MnOOH}$  were refluxed under boiling conditions in 100 mls of 4M  $\text{LiOH}$  solution for 6 hours. Some of the suspension was poured into a centrifuge tube and settled by centrifugation. The liquid was then decanted, leaving minimal residual salt solution behind, and the resulting wet powder directly heated in an alumina boat to  $200^\circ\text{C}$  in flowing argon. Figure 6 shows the x-ray diffraction pattern for this material showing that it is basically identical in a structural sense to the materials shown in comparative example 1, even though it has been prepared under strikingly different conditions.

A  $\text{Li/LiMnO}_2$  test cell was prepared from this material. Figure 7 shows the voltage-capacity relation for this cell, which obtains 180 mAh/g between 4.2 and 2.0 V.

This example demonstrates that excellent  $\text{LT-LiMnO}_2$  material for use as cathodes in lithium batteries can be made using the invention process. Material similar to that described in the prior art can be prepared at temperatures as low as  $200^\circ\text{C}$ .

##### Example 2:

3.0 grams of  $\gamma\text{-MnOOH}$  was added to 100 mls of 4M  $\text{LiOH}$  solution. The mixture was refluxed by boiling for 6 hours. The solids were collected by filtering, and rinsed in water several times. The resulting powder was dried at  $120^\circ\text{C}$  in vacuum. Figure 8 shows the diffraction pattern for this sample. A comparison with Figure 3 shows that a structurally identical product (apart from small impurity peaks near 18.7, 26, 26.9, 33.1 and 38.6 degrees) has been prepared.

A  $\text{Li/LiMnO}_2$  test cell was prepared using this material. Figure 9 shows the voltage-capacity relation for this cell. This cell obtains 190 mAh/g between 4.2 and 2.0 V after the first charge in good agreement with the cells described in comparative example 1. However, the capacity of the first charge is only about 160 mAh/g showing that insufficient Li has been incorporated in the material by the ion exchange followed by rinsing in water. Some Li was removed by "reverse ion-exchange" with hydrogen during the rinsing steps. Therefore, this material must be considered  $\text{Li}_x\text{H}_{1-x}\text{MnO}_2$  with x near 0.88 after this rinsing.

This example demonstrates a means of varying the degree of lithiation while otherwise preparing the same

to those for Cu K $\alpha$ . This is done using standard methods (B.D. Cullity, "X-Ray Diffraction", Addison-Wesley, 1969). Table 1 gives the Bragg Peak positions and integrated peak intensities for LiMnO<sub>2</sub> as prepared at about 1000°C (Dittrich and Hoppe, Z. Anorg. Allg. Chemie 368, 262 (1969)). Although LiMnO<sub>2</sub> prepared at this temperature is not electrochemically equivalent to compounds of similar stoichiometry prepared at lower temperatures, the x-ray patterns are similar enough for purposes of identifying impurity related peaks in the patterns. From a comparison of Figure 3, Table 1 and said reference, it is clear that the material prepared by the invention methods is more pure than that of said Ohzuku et al. reference.

**TABLE 1**  
**LITERATURE DIFFRACTION PATTERN FOR LiMnO<sub>2</sub>**

MILLER INDICES	SCATTERING ANGLE	RELATIVE INTENSITY
010	15.264	50
011	24.571	56
110	35.408	23
021	36.742	18
101	37.360	12
002	39.169	75
111	40.605	39
012	42.401	20
120	44.902	100
030	47.227	7
102	51.501	8
112	53.989	17
130	58.113	18
122	61.344	95
131	62.027	29
032	63.106	10
040	64.777	20
200	66.708	21
210	68.881	11

A Li/LT-LiMnO<sub>2</sub> test cell was assembled from this powder. The cell was charged and discharged using currents of 5.7 mA/g. The cell voltage versus capacity for the first three cycles is shown in Figure 4. The specific reversible capacity for this cell over the first three cycles is greater than 170 mAh/g between 2.0 and 4.2 V. Other similar cells obtained equal or better performance. This performance is equal to that shown in said reference (Figure 2 in this reference). Similar cells cycled between 2.0 and 3.8 V at the same specific current obtained 120 mAh/g of reversible capacity for over 30 charge discharge cycles.

**Example 2:**

X-ray pattern information for LiMn<sub>2</sub>O<sub>4</sub> was obtained from the literature (Natl. Bureau of Standards (U.S.) Monograph 25, 2178, (1984) and Joint Commission on Powder Diffraction Standards (JCPDS) reference database. Peak positions and relative intensity are shown in Table 2.

that of a wound type Li ion rechargeable battery shown in Figure 1. Cathode foils are prepared using lithium manganese oxide powder, a binder, and a conductive dilutant mixture applied to a thin aluminum foil. Anode foils are prepared using suitable carbonaceous compound mixtures and a binder applied to a thin copper foil. A dry cell assembly 4 is then prepared by spirally winding an anode and cathode segment together into a "jelly roll" with two microporous polyolefin film sheets acting as separators. Typically, anode foils are slightly wider than the cathodes as indicated by anode edges 12, 15 and cathode edges 13, 14 in Figure 1. The "jelly roll" is inserted into conventional cylindrical battery containers 3. Appropriate insulating pieces 2,7 are included and tab connections 5,6 are made to the cell case 3 and header 1. Safety devices may be included as desired. Figure 1 shows the use of a combination safety vent and pressure operated disconnect device (in the header 1) that may be employed. Electrolyte 8 consisting of a suitable lithium salt in a mixture of non-aqueous solvents is added to activate the battery prior to crimping the header-case assembly shut.

For illustrative and/or comparative purposes, other lithium manganese oxide samples were synthesized in the examples to follow using the same reactants and a conventional synthesis method. Pellets of mixed  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\gamma\text{-MnOOH}$  powders were made using a hardened steel pellet press operated with a pressure on the powders of about 1000 bar. A Retsch Model RM-0 automatic grinder was used to thoroughly mix the reactants. Heating of the pellets was performed using the same apparatus and methods employed in the invention process.

In the examples to follow, a Phillips powder diffractometer equipped with a Copper target x-ray tube and a diffracted beam monochromator was used for diffraction measurements. A TA instruments Model 951 thermogravimetric analyzer was used when monitoring the reaction between  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\gamma\text{-MnOOH}$  solids.

Laboratory test cells were employed to illustrate the electrochemical behaviour of the lithium manganese oxide cathode materials that were prepared. These cells used an anode of lithium metal which acts as a useful reference electrode for this purpose. The information provided from such cells allows those skilled in the art to engineer suitable lithium ion batteries with these materials as cathodes. The laboratory test cells were constructed as shown in Figure 2. 2325 size coin cell hardware, comprising negative container 21, gasket 22, and positive container 30, equipped with a spacer plate 24 (304 stainless steel) and a disc spring 23 (mild steel) was used as the test vehicle. A special corrosion resistant grade of stainless steel was used for the positive container hardware 30 to prevent oxidation. The disc spring 23 was selected so that a pressure of about 15 bar would be applied to each of the cell electrodes (anode 25 and cathode 27) when the cell was crimped closed. 125 $\mu\text{m}$  thick Li foil was used as the anode 25 in these cells. The separator 26 was Celgard<sup>TM</sup> 2502 microporous film which had been wetted with electrolyte 28 consisting of 1M  $\text{LiPF}_6$  dissolved in a 50/25/25 volume percent mixture of Dimethyl Carbonate, Propylene Carbonate and Ethylene Carbonate respectively. Cathodes 27 were made from the lithiated manganese oxide powder, Super S carbon black (10% by weight) and polyvinylidene (PVDF) binder, uniformly coated on aluminum foil. The lithiated manganese oxide and the carbon black were added to a solution of 20% PVDF in N-methylpyrrolidinone (NMP) such that 10% of the final electrode mass would be PVDF. Excess NMP was then added until the slurry reached a smooth syrupy viscosity. The slurry was then spread on the Al foil using a doctor blade spreader and the NMP evaporated at about 90°C in air. Once the electrode stock was dried it was compressed between flat plates at about 25 bar pressure. Test electrodes of dimension 1.2cm x 1.2cm were then cut from the electrode stock using a precision cutting jig. These electrodes were then weighed and the weight of the foil, the PVDF and the carbon black were subtracted to obtain the active electrode mass.

All cell construction and sealing was done in an Argon-filled glove box. After construction, the cells were removed from the glove box and cycle tested using constant current cyclers. Currents were adjusted to be 5.7 mAh/gram of active material.

## Comparative Examples

### Example 1:

6.554g  $\gamma\text{-MnOOH}$  and 3.445g  $\text{LiOH}\cdot\text{H}_2\text{O}$  were thoroughly mixed together using the automatic grinder. A 10% atomic stoichiometric excess of Li was included, ie: the Li:Mn ratio in the mixture was 1.1:1. After mixing, the powders were pressed into a pellet at 1000 bar pressure. The pellet was then tightly wrapped in Ni foil. The wrapped pellet was placed in an alumina boat and then heated under flowing argon for 18 hours at 350°C. After heating it was reduced to powder by grinding and analyzed by x-ray diffraction. Figure 3 shows the diffraction pattern obtained. This pattern agrees well with that of similar material prepared by T. Ohzuku et al., J. Electrochem. Soc. 137, 769, (1990). (shown in this article's Figure 1) except that, in their work, the impurity peak near 18°, belonging to the pattern for  $\text{LiMn}_2\text{O}_4$ , is of equal height to the 011 peak at 24.5°. (Note that the data in this reference was collected using Fe K $\alpha$  radiation, so the angles there must be corrected to correspond

In the following, solid solution materials containing a uniformly dispersed mixture of one or more solid substances at the ionic level are normally referred to as  $A_xB_yMO_z$  where x, y, and z refer to the ranges of elements A, B, and O present with respect to the element M. Valence restrictions limit the theoretical ranges possible for these parameters. A person skilled in the art will understand the interdependence of and the absolute ranges possible for these parameters. Also in the following, the term low temperature is used to mean below 300°C to clearly distinguish it from the prior art.

Ion exchange is defined by Grimshaw and Harland, ("Ion Exchange: Introduction to Theory and Practice" Published by: The Chemical Society, London, England, 1975), as "the reversible interchange of ions between a solid phase (the ion-exchanger) and a solution phase; the ion-exchanger is usually insoluble in the medium in which the ion exchange is carried out". If an ion exchanger  $M^+A^+$  carrying  $A^+$  cations is placed in an aqueous solution containing  $B^+$ , an ion exchange reaction takes place represented by the following equation:



The anion in solution usually does not take place in the exchange to any appreciable extent. In the examples of this invention, M can be identified with  $MnOO$ , A with H, Na, K, etc. and B with Li.

Ion exchange reactions are generally topotactic. In this relatively gentle reaction, the structure of the framework is retained while mobile ions of one type ( $H^+$  in the examples to follow) are exchanged for those in high concentration in solution ( $Li^+$  in the examples). Therefore, one can expect the structure of the ion exchanged product to mirror that of the starting reactant.  $MnOOH$  exists in three well documented forms. There is the  $\gamma$ - $MnOOH$  form used here, called manganite, described in M.J. Buerger, Zeitschrift fur Kristallographie 95, 163 (1936), and in D.Glover, B. Schumm, Jr. and A. Kozawa, "Handbook of Manganese Dioxides, Battery Grade" Published by the International Battery Materials Association (1989) page 6, which shows structural similarity to orthorhombic  $LiMnO_2$ . There is  $\alpha$ - $MnOOH$ , called groutite, and  $\beta$ - $MnOOH$  called Feitknechtite (D.Glover, B. Schumm, Jr. and A. Kozawa, "Handbook of Manganese Dioxides, Battery Grade" Published by the International Battery Materials Association (1989) page 6, and/or Owen Bricker, The American Mineralogist, 50, 1296 (1965). The former takes a ramsdellite-type structure and the latter is apparently a layered structure like  $Mn(OH)_2$ . The inventors expect the synthesis methods to be applicable to each of these  $MnOOH$  starting materials and that useful materials as cathodes in Li-ion cells will be produced. Furthermore, it is likely that  $Mn(OH)_2$  can also be ion-exchanged using our methods, again producing useful electrode materials for Li-ion cells. A summary of present and expected results is shown in the following table.

Starting Materials	$\alpha$ - $MnOOH$	$\beta$ - $MnOOH$	$\gamma$ - $MnOOH$	$Mn(OH)_2$
Common Name	Groutite	Feitknechtite	Manganite	Manganese Hydroxide
Structure Type	Ramsdellite	Layered	Manganite	$Cd(OH)_2$ Type
After Ion Exchange	? (X-phase Type)	?	$Li-Li_{1-x}MnO_2$	? ( $Li_2NiO_2$ -Type)
After Heating Becomes	?	?	$Li-LiMnO_2$ for $x > 0.9$ $LiMn_2O_4$ for $x < 0.5$	?

Lithium manganese oxide is prepared using a two-stage process.  $\gamma$ - $MnOOH$  obtained from Chemetals (Baltimore, Md., USA) and  $LiOH \cdot H_2O$  obtained from FMC (Bessemer City, NC., USA) were used as reactants. Lithiation was accomplished by stirring  $\gamma$ - $MnOOH$  in aqueous  $LiOH$  solution at about 100°C in a refluxing set-up. A variety of post-lithiation treatments to dry the powder can be employed and include filtering, settling, and, centrifuging in addition to heating. Heating is performed in tube furnaces equipped with stainless steel furnace tubes above 120°C. The ends of the furnace tubes could be closed by flanges with gas flow or vacuum fittings so that heating could be done under air, inert gas, or vacuum.

Primary or rechargeable lithium batteries are then constructed employing the lithium manganese oxide material as a cathode material (either as the major component or as an additive). A preferred construction is



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